The Crystal Structure of Diamminecadmium(II) Tetracyanoniccolate(II) Benzene Clathrate, $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$*[1]

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During the course of our studies on "Hofmann-type" benzene clathrates, $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ where M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), or Cd(II) and M'=Ni(II), Pd(II) or Pt(II),[1] it was assumed that these complexes would have structures similar to that of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ known as Hofmann's clathrate.[2] And it was considered highly desirable to carry out additional studies using single crystals.

The present communication reports results of the crystal structure determination which proved the above mentioned structure in the case of M=Cd and M'=Ni which has been already subjected to IR[3] and NMR[4] studies.

The crystals are tetragonal, with the space group of $P_{4/m}$-C'_{4h}. One formula unit is contained in a cell of the dimension: $a=b=7.575\pm0.006$ Å and $c=8.317\pm0.005$ Å. No piezo-electricity was observed.

The intensities of the three-dimensional reflections were measured visually from equi-inclination Weissenberg photographs around the a and c axes taken with Ni-filtered Cu$K\alpha$ radiation. In total, 356 reflections were collected. Table 1 shows the atomic parameters which give the R-factor of 11.8%.

On the whole, the crystal has a lameller structure, inorganic polymer sheets and layers of benzene being alternated. As shown in Fig. 1, the cadmium atom at 0, 0, 0 and the nickel atom at 1/2,1/2,0 are joined together by cyanide bridges to form planar sheets parallel to the plane (001). Four nitrogen atoms of cyanide anions and two ammonia molecules at *trans*-positions coordinate to a cadmium atom forming an octahedron. Four carbon atoms of cyanide ligands take square planar configuration in a $Ni(CN)_4$ unit. Benzene molecules are arranged between these sheets with their molecular planes parallel to the c axis making an angle of 58°30′ to a or b axis.

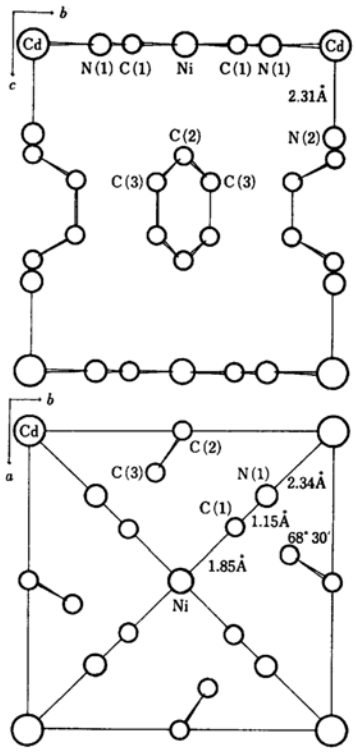

Fig. 1. Projections of the unit cell along a and c axes.
The standard deviations of the bond lengths are 0.03 Å for C-N and Cd-NH_3 and 0.02 Å for Ni-C and Cd-N(C).

TABLE 1. ATOMIC PARAMETERS WITH STANDARD DEVIATIONS

	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	B(Å^2)
Cd	0000(0)	0000(0)	0000(0)	0.472(0.039)
Ni	5000(0)	5000(0)	0000(0)	1.909(0.108)
C(1)	3276(29)	3261(29)	0000(0)	1.422(0.368)
C(2)	0000(0)	5000(0)	3410(59)	4.451(0.267)
C(3)	1427(55)	4153(58)	4179(50)	7.447(0.891)
N(1)	2203(29)	2180(29)	0000(0)	2.389(0.409)
N(2)	0000(0)	0000(0)	2777(37)	1.804(0.466)

The electron clouds of the benzene molecules seem to be closely packed and are almost in contact with each other. These layers thus can be regarded as two-dimensional crystals of benzene between inorganic polymer sheets, $[Cd(NH_3)_2Ni(CN)_4]_\infty$.

*[1] The Metal Ammine Cyanide Aromatics Clathrates. VIII

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